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**PHOTOPRODUCTION OF DISORDER IN
PB(N₃)₂ AND TIN₃**

D. A. WIEGAND

DECEMBER 1970

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Technical Report 4080

PHOTOPRODUCTION OF DISORDER IN
 $\text{Pb}(\text{N}_3)_2$ and TlN_3

by

D. A. Wiegand

December 1970

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DA Project 1T061102A32B
AMCMS Code 501B.11.856

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ABSTRACT

Pb, Tl, and other inorganic azides have been exposed to ultraviolet and X-ray irradiation, and the resulting changes in optical properties have been studied. This irradiation was found to produce a structureless increase in extinction, which increases in magnitude with decreasing wavelength to the band edge. Calculations for $\text{Pb}(\text{N}_3)_2$ indicate that the wavelength dependence of this irradiation-induced extinction is what might be expected from colloidal lead. The increased extinction is insensitive to the temperature of observation, and diffuse reflectance measurements indicate that some part, if not all of it, is due to absorption. Both of these results are to be expected if the extinction is due to colloidal lead. Essentially the same type of extinction is obtained for ultraviolet and X-ray irradiation at sample temperatures of 120°, 780°, and ~ 300°K, and also for decomposition produced solely by thermal means. Some differences between $\text{Pb}(\text{N}_3)_2$ and TlN_3 are discussed.

INTRODUCTION

The inorganic azides are very sensitive to various forms of radiation, e.g., ultraviolet light and X-rays (Ref 1). The azide ion, N_3^- , is a linear array of three nitrogens, which breaks up upon electronic excitation. Many point imperfections have been detected in the alkali azides by electron spin resonance. These have been produced by irradiation and include N^0 , N_2^- , N_3^{--} , N_4^- , and the F center (Ref 1,2,3,4,5). Many optical bands also are produced by irradiation; the spectra resemble those obtained from various kinds of glass and quartz and, to some extent, the alkali halides (Ref 1,7,8). These optical bands suggest a variety of pointlike defects, and there has been some success at correlating a few of the bands with the defects detected by electron spin resonance, e.g., the N_4^- (Ref 6).

In contrast to the alkali azides, some of the heavier metal azides, e.g., Pb, Tl, and Ag, do not show evidences of pointlike defects on irradiation (Ref 9,10,11). No molecular defects have been observed in these azides by spin resonance, and the optical spectra exhibit very little structure. $Ba(N_3)_2$ may be an intermediate case since it exhibits some properties of both of these groups of azides. Thus some of the molecular defects have been observed by spin resonance in this azide (Ref 2,12), but the optical properties following irradiation are more similar to those of the heavier metal azides (Ref 9,10). However, all of these azides, within the room temperature range, evolve nitrogen gas on irradiation and so decompose under the influence of radiation (Ref 1). The work reported on in this paper is concerned with the disorder generated in the heavier metal azides, e.g., Pb, and Tl as a result of irradiation.

EXPERIMENTAL

Samples for optical measurements have been grown from solutions; e.g., $Pb(N_3)_2$ was grown from a saturated solution of ammonium acetate by slow cooling (Ref 13). Visual and optical observations indicate reasonably good but small single crystals. TlN_3 samples were grown from aqueous solutions either by evaporation or by slow cooling. The samples were in general small, polycrystalline, and not clear. The small size of both $Pb(N_3)_2$ and TlN_3 samples and the light-scattering properties of TlN_3 , which were most probably due to internal boundaries, made optical measurements rather difficult and decreased their precision considerably.

Samples were exposed either to ultraviolet light or to X-rays. The ultraviolet light was obtained from a high-pressure Hg lamp, and filters were used to give primarily the 3650Å line. In a few cases, samples were exposed to unfiltered light from the Hg source or from the I.R. #2 tungsten lamp source of the Cary Spectrometer. X-rays were obtained from a source operating at 30 kvp and 20 ma or another source operating at 50 kvp and 40 ma. An Al filter was used to remove the softer X-rays from the beam.

For irradiation and measurements at low temperatures samples were mounted in a standard vacuum cryostat manufactured by Sulfrian, Inc., Rahway, N.J. For measurements at room temperature samples were mounted either in the vacuum cryostat or in air. Temperature measurements were made using a platinum resistor and a Cryotronics resistance bridge. The platinum resistor was secured to a copper block which served as a base for attaching the sample holder. All temperatures reported are those of the platinum resistor. In addition, the term "300°K" is used very loosely to mean room temperature. This temperature was in many cases unmeasured. For mounting in the cryostat the sample was glued with Duco cement to a copper plate (sample holder) which was bolted onto the copper block. Optical absorption measurements were made with a Cary Spectrophotometer, Model 14R, diffuse-reflectance measurements with a Perkin-Elmer Spectrophotometer, Model 350. Most of the optical data are given in terms of optical density which is defined as

$$\log_{10} \frac{I_0}{I_T}$$

where I_0 and I_T are the incident and the transmitted intensities. It is important to note that attenuation of the beam on passing through a sample can be due to absorption and/or scattering, and the term extinction is used to denote both. Because of the high absorption coefficient of the samples for X-rays and ultraviolet light, defects are not produced throughout the whole volume of the sample. Thus it is not possible, even in cases where the extinction is due only to absorption, to convert optical density into an absorption coefficient.

RESULTS AND DISCUSSION

Irradiation-Induced Changes in Optical Transmission

In Figures 1 and 2 typical results are given for $\text{Pb}(\text{N}_3)_2$ and TlN_3 (Ref 9, 10). The abrupt increase in optical density at about 4050Å for $\text{Pb}(\text{N}_3)_2$ and 4300Å for TlN_3 is due to the absorption edge. Figures 1 and 2 indicate that exposure to irradiation causes a structureless change in extinction which increases monotonically with decreasing λ from the red to the blue. The tendency of the difference curve for TlN_3 (Fig 2) to flatten at about 4400Å is not always observed, and often the results are similar to those given for $\text{Pb}(\text{N}_3)_2$ in Figure 1. Results of this type are illustrated for TlN_3 in Figure 3. The change in optical density shown in Figure 3 is due to a longer irradiation time than the change shown in Figure 2. In Figure 4 results are given for a TlN_3 sample which has received a prolonged exposure to X-rays. It is to be noted that the change in optical density given in Figure 4 is considerably larger than the changes given in Figures 1, 2, and 3. The data of Figure 4 are presented to show that the structureless increase in extinction extends far into the infrared.

A structureless increase in extinction of the type illustrated in Figures 1, 2, and 3 can be produced in KN_3 by irradiation and subsequent heat treatment. The extinction in this case may, however, be due to surface scattering. Attempts to produce this type of extinction in NaN_3 by irradiation and heat treatment were not successful. Irradiation of $\text{Ba}(\text{N}_3)_2$ produces discrete absorption bands which may be superimposed on a structureless increase in extinction of the type found in TlN_3 and $\text{Pb}(\text{N}_3)_2$. Further work is necessary to clarify the results for both $\text{Ba}(\text{N}_3)_2$ and KN_3 .

The data presented in Figures 5, 6, 7, and 8 indicate that essentially the same results are obtained when $\text{Pb}(\text{N}_3)_2$ is exposed to ultraviolet light or X-rays at 120°, 780° or 300°K. The data for these four figures were chosen to have approximately the same optical density so that comparisons could easily be made. The irradiation dose is not necessarily the same in each case (see Fig 14 and 15 and related discussion). Most of the differences in the curves of Figures 5, 6, 7, and 8 are within the range of variations from sample to sample and even from measurement to measurement on the same sample. Examination of TlN_3 with a low power microscope reveals that the samples are

not uniformly colored. This nonuniformity of coloration, coupled with the small sample size and the difficulty of reproducing the exact position of the sample in the spectrophotometer beam, most probably accounts for most of the differences between the curves in Figures 5, 6, 7, and 8. In addition, scattering from small surface and volume irregularities further causes the results to be very sensitive to the position of the sample in the spectrophotometer beam. Some of the differences between these curves may, however, be significant, and this problem is considered further below.

When TlN_3 is exposed to ultraviolet light at 120°, 800°, and 300°K the results are similar to those given in Figure 5. In addition, there is little difference in the results for TlN_3 exposed to ultraviolet light or X-rays at 300°K. However, when TlN_3 is exposed to X-rays at 80°K, the effect is somewhat different. As shown in Figure 9, in this case there is a band at about 5500Å superimposed on the structureless change in optical density characteristic of other conditions. This band at about 5500Å anneals on warming to 300°K. For comparison purposes the change in optical density due to ultraviolet irradiation at 80°K is given in Figure 10. This band suggests the presence of point defects due to irradiation.

Colloidal Metal Production

As noted in the Introduction, lead and thallous azides evolve N_2 gas when exposed to ultraviolet light at temperatures in the vicinity of room temperature (Ref 1). In this investigation it has been found that gas, presumably nitrogen, is given off when TlN_3 is exposed while at temperatures slightly above that of liquid nitrogen. These facts, plus the lack of evidence for point defects under most conditions as a result of irradiation, suggest that colloidal metal may be formed during irradiation as is the case in the silver halides (Ref 14) and in silver azide (Ref 11). Thus the change in optical density may be due to colloids. Preliminary calculations of the absorption due to colloidal Pb have recently been carried out by M. Barkey and T. Gora of this Laboratory (Ref 15). They have used the Mie Theory for a low density of small (diameter < 250Å) spherical particles. The results (Fig 11) indicate a structureless absorption which increases in going from the red to the blue in general agreement with experiment. Unfortunately, the optical constants for Pb, which are available, do not vary smoothly with wavelength

as expected. This probably is due to surface contamination, and variation in conditions from one laboratory to another, plus the fact that the measurements were made many years ago. In making their calculations Barkey and Gora assumed that the optical constants for Pb vary smoothly with λ , and so they fitted a smooth curve to the experimental points. In addition, the optical constants for $\text{Pb}(\text{N}_3)_2$ are not available, so that the calculations are for Pb in matrices of material having a few arbitrarily chosen values of the index of refraction, which do not vary with λ . Since the observations are in the vicinity of the absorption edge of $\text{Pb}(\text{N}_3)_2$, the optical constants will be wavelength-dependent. Because of limitations caused by the lack of optical data for Pb and $\text{Pb}(\text{N}_3)_2$, detailed comparisons of the calculations of Barkey and Gora with the experimental results are not warranted. Their calculations do, however, indicate that the observed changes in extinction may be due to colloidal lead. It then is possible that some of the differences in the curves of Figures 5, 6, 7, and 8 may be due to differences in the shape and size of colloidal Pb particles (Ref 16). It also is quite possible that the particle size, in particular, may depend on sample temperature during exposure and also on the density of ionization produced during irradiation. Since the absorption coefficients for ultraviolet light and for X-rays are markedly different, the resultant densities of ionization also are considerably different. The mechanisms for the production of colloidal metal during irradiation is not clear, especially at low temperatures where diffusion is not expected to be probable.

It is interesting to consider the optical properties of colloidal metal in addition to those already discussed. The extinction due to colloidal metal should be insensitive to the measurement temperature (Ref 17). In Figure 12 the optical density of a TlN_3 sample irradiated at 80°K is given for measurements at 80° and 300°K. The sample was heated to 300°K for measurement after exposure, and then recooled to 80°K for another measurement. Thus any possible annealing effects caused by the first heating have been eliminated. It is clear that the extinction is insensitive to temperature, as expected for colloidal metal.

The extinction due to colloidal metal should be composed of a component due to absorption and a component due to scattering (Ref 16), and the importance of the scattering component will depend on particle size. In addition, inclusions of nitrogen could be expected to cause scattering,

but no appreciable absorption (Ref 16). Since nitrogen is known to escape during irradiation, it is not unreasonable to expect inclusions or bubbles of gas to remain in the sample. Thus an extinction which is due largely to scattering suggests inclusions of nitrogen, while extinction which has a significant component due to absorption will support the hypothesis that it is due to colloidal metal. In the latter case, a comparison of the relative magnitudes of the scattering and absorption components may give information about the particle size. In an effort to determine whether a component of the extinction is due to absorption, measurements have been made of changes in the diffuse reflectance due to irradiation. Powdered samples have been used, and the diffusely reflected light was collected by integrating spheres.

Results of diffuse reflectance measurements on unirradiated and irradiated TlN_3 are given in Figure 13. This type of measurement is insensitive to the scattering of light by imperfections, since the scattered light is collected by the integrating spheres independently of whether it is diffusely reflected or scattered by imperfections. However, energy which is absorbed by the powder is not collected by the spheres. The relationship between the diffuse reflection and the absorption coefficient is not simple, but it is monotonic (Ref 18), and a decrease in diffuse reflectance indicates an increase in absorption. The sharp decrease in diffuse reflectance (Fig 13) of the unirradiated material at about 4300Å is due to the fundamental absorption edge. The data of Figure 13 show that there is a structureless decrease in diffuse reflectance of the irradiated material which increases in magnitude on going from the red to the blue. Thus there is a structureless increase in absorption due to irradiation which increases on going from the red to blue. Hence the increase in absorption coefficient due to irradiation is, in wavelength dependence, very similar to the increase in extinction. From these measurements it is possible to conclude that part of the change in extinction is due to a change in absorption. This conclusion supports the hypothesis that colloidal metal is produced by irradiation. Additional measurements are necessary to determine if a significant part of the extinction is due to scattering.

Kinetics of Defect Production

The data of Figures 9 and 10 indicate differences between ultraviolet and X-ray irradiation for TlN_3 , which

the data of Figures 5, 6, 7, and 8 fail to do for $\text{Pb}(\text{N}_3)_2$. There are, however, differences in the kinetics of defect production in $\text{Pb}(\text{N}_3)_2$ for ultraviolet and X-ray irradiation. These are illustrated in Figures 14 and 15.

The data of Figure 14 show that the efficiency of defect production for ultraviolet irradiation decreases appreciably on going from 300°K to 78°K, while Figure 15 shows a slight increase¹ in this efficiency for X-ray irradiation and the same temperature change. In addition, the curves of Figure 14 for ultraviolet irradiation show saturation characteristics with irradiation time, while Figure 15 indicates that the growth is linear for X-ray irradiation. These differences may be due to the difference in ionization density produced by the two types of irradiation. For ultraviolet irradiation the disorder is produced in a very thin surface layer, and the density of imperfections is much higher than for x-ray irradiation. Thus the saturation character of the growth curves of Figure 14 may be due to exhaustion of the sources of imperfections. Alternately, back reactions which are ionization density dependent may account for the different functional forms of the curves in Figures 14 and 15. While detailed data of the type of Figures 14 and 15 are not available for TlN_3 , it has been observed that the efficiency of defect production decreases with decreasing temperature for ultraviolet irradiation.

Annealing

When TlN_3 is irradiated at low temperature and then heated to room temperature, the only change in the optical density is due to the annealing of the small band at $\sim 5500 \text{ \AA}$ (Fig 9) for X-ray irradiation. There is no change for ultraviolet irradiation. In contrast, if $\text{Pb}(\text{N}_3)_2$ is irradiated at a low temperature and heated to room temperature, essentially all of the induced change in extinction is annealed out in two or more annealing stages. One of these stages is in the vicinity of 78°K and is illustrated by the vertical arrows at the upper curve of Figure 15. Thus in $\text{Pb}(\text{N}_3)_2$ it apparently is possible to reverse the irradiation-induced slow decomposition process by thermal

¹The position of the sample in the spectrometer beam is changed slightly on cooling from 300°K to 78°K. Hence, slightly different parts of the sample are measured at the two temperatures, and the small differences in slopes for the two temperatures, Figure 15, may be due to this change in position.

treatment if the irradiation has been carried out at low temperatures.

Thermal Decomposition

This report is primarily concerned with slow decomposition produced by irradiation. The data of Figure 16, however, show that essentially the same wavelength dependence of the change in optical density can be produced by heat treatment. Thus, colloidal metal also may be produced during thermal decomposition. This conclusion is not surprising in view of the fact that N_2 gas is also given off during thermal decomposition (Ref 1). Examination with a low power microscope reveals that the damage is apparently closer to the surface when thermally induced than when irradiation-induced.

SUMMARY AND DISCUSSION

The results to date support the hypothesis that the structureless increase in optical extinction due to irradiation of $Pb(N_3)_2$ and TlN_3 is attributable, at least in part, to colloidal metal. The calculations of Barkey and Gora give results which are not inconsistent with experiments; the extinction is insensitive to temperature as expected for colloids; and, finally, the diffuse scattering measurements show that at least part of the extinction is due to absorption. It is not possible at this time, however, to rule out the possibility that some part of the extinction is due to scattering from "colloidal" nitrogen or from compounds of nitrogen. To investigate this question, it will first be necessary to determine if a significant part of the extinction is due to scattering. If these additional experiments show that the extinction is exclusively due to absorption, it will be possible to rule out nitrogen or nitrogen compounds, since these are not expected to give appreciable absorption in comparison with scattering. It then may also be possible to place an upper limit on the colloidal metal particle size (Ref 16). If, on the other hand, an appreciable component of the extinction is found to be due to scattering, it will be necessary to use other approaches to distinguish between colloidal metal and nitrogen. The calculations will be further pursued in an effort to better characterize what might be expected from various types of colloids. If better and more complete data on optical constants can be found, a detailed comparison between calculations and experiments will be made.

It may be possible to distinguish between the various types of colloidal material in this manner.

A preliminary but unsuccessful search has been made for the spin resonance of conduction band electrons in colloidal metal in irradiated TlN_3 . The work to date is not complete and further experiments will be carried out. A conduction electron spin-resonance signal which is correlated with the optical results gives one of the most convincing arguments for the presence of colloidal metal (Ref 19,20). There are, however, reasons why a signal may not be observed even in the presence of colloidal metal.

One of the most interesting parts of this work arises out of the possibility of colloid production at low temperatures, e.g., 78° and 120°K, due to exposure to irradiation. Diffusion of the type necessary to produce colloids is generally not observed and not expected in nonmetallic systems at these low temperatures. While colloidal metal is produced in the silver halides and, in some cases, in the alkali halides by irradiation, in the vicinity of room temperatures, it is not produced, or at least not very efficiently produced, at low temperatures. A minimum condition for metal-colloid production might be that metal atoms or ions must be able to move over short distances, e.g., a few lattice parameters, so as to cluster. Alternately, the nitrogen must move out of a region so that the remaining metal ions plus the appropriate number of electrons can collapse into metallic colloids. Similar conditions are necessary for the production of nitrogen colloids. The necessary diffusion may take place only during irradiation if, for example, the charged state of the metal or nitrogen which diffuses exists only in the presence of radiation.

The observation for TlN_3 that the coloration is non-uniform across the sample strongly indicates that the mechanism of disorder production is very sensitive to sample perfection. The process may be sensitized by chemical or mechanical imperfections as is the case in the silver halides (Ref 14). Imperfections may act as nucleation centers for colloidal production, or they may simply influence the trapping and the lifetimes of electrons, holes, and excitons, and so affect the efficiency of other processes which are dependent on the presence of these electronically excited states. The efficiency of defect

production in alkali halides is strongly dependent on chemical and mechanical perfection (Ref 17,21). Comparisons are made here only between the heavy metal azides and a few other materials in which it is established that the disorder is produced by mechanisms involving only electronic excitation and ionization (Ref 17,21). In many materials, disorder is produced only by radiation sufficiently energetic to produce displaced atoms or ions by collision processes. It may be possible to understand the mechanisms of disorder production in azides by kinetic studies such as those shown in Figures 14 and 15 as a function of sample perfection and also as a function of such phenomena as irradiation intensity and sample temperature.

It is interesting to note that the alkali azides resemble the alkali halides in several respects, while the heavy metal azides are similar to the silver halides. In both the alkali azides and the alkali halides a variety of pointlike imperfections is produced by ionizing radiation. In contrast, pointlike imperfections have not been observed, as a result of irradiation, in the heavy metal azides or in the silver halides. It appears that only colloidal metal is produced, by ionizing radiation, in the heavy metal azides and in the silver halides. The band gaps of the alkali azides and the alkali halides are of the same order of magnitude, and are considerably larger than those of the heavy metal azides, which in turn are similar to those of the silver halides (Ref 1,14). In addition, the indices of refraction of the alkali azides and the alkali halides are similar in magnitude, and are appreciably smaller than those of the heavy metal azides which are again similar to those of the silver halides (Ref 1,14). This difference may have an important bearing on whether or not certain types of point defects are stable. The larger the index of refraction, the smaller will be the binding energy of electrons and holes to charged defects such as vacancies, other conditions being equal. Because of the smaller binding energy there is thus a smaller probability that this type of defect will be stable. It is therefore possible that some of the differences between the alkali azides and alkali halides on the one hand and the heavy metal azides and the silver halides on the other in regard to stable disorder produced by irradiation are attributable to the differences in the indices of refraction.

It also may be possible that the mechanisms of defect production by ionizing radiation in the alkali azides and halides have similarities and that these mechanisms in

the heavy metal azides are in some ways similar to those in the silver halides. Unfortunately, nothing is known about the intrinsic disorder in any of the azides, and very little about diffusion. Diffusion is important in the photographic process, i.e., in the formation of colloidal silver during irradiation of the silver halides (Ref 14), and may be important in the formation of colloidal metal in the heavy metal azides. In addition, the type of disorder produced by irradiation may at least in part be determined by the type of intrinsic disorder, e.g., the role of interstitial silver, which is an intrinsic type of disorder in the silver halides in the formation of colloidal silver (Ref 14). In this respect it would be very helpful to know if interstitial metal is an intrinsic form of disorder in the heavy metal azides.

Finally, it is interesting to speculate on a possible use of materials which are photosensitive at low temperatures. Preliminary experiments with powders indicate that both TlN_3 and AgN_3 are more photosensitive than $AgCl$ at $80^\circ K$. It might therefore be useful to consider the possibility of employing either TlN_3 or AgN_3 as the photosensitive component of an emulsion to be used at low temperatures. For either of these materials to be of practical use in this respect it will most probably be necessary to find some means of "developing", since the high efficiency of the silver halides arises because of the developing process (Ref 14).

ACKNOWLEDGEMENTS

The author is indebted to Dr. Harry D. Fair for assistance in making magnetic resonance measurements, to Mr. Arthur Forsyth for assistance in the studies of gas evolutions, to Mr. Wayne Garrett and Dr. Jagadish Sharma for providing samples, and to Pvt. Mark Barkey and Cpt. Thaddeus Gora for making the result of their calculations available. The author also appreciates the assistance rendered by the above and other members of the Explosives Laboratory, FRL, Picatinny Arsenal, in making equipment available, and in many helpful discussions.

REFERENCES

1. A.D. Yoffe, Developments in Inorganic Nitrogen Chemistry, Elsevier, Amsterdam (1966)
2. P.L. Marinkas, and R.H. Bartram, ESR of N_2^- in UV-Irradiated Single Crystals of Anhydrous Barium Azide, J. of Chem. Phys. 48, 927 (1968)
3. P.L. Marinkas, ESR Studies of N_3^{--} and N_2^- Molecular Ions in Anhydrous Barium Azide, J. Chem. Phys., To Appear 15 May 1970.
4. G.J. King, F.F. Carlson, B.S. Miller, and R.C. McMullan, Evidence of Trapped N Atoms in X-Ray Irradiated NaN_3 , J. Chem. Phys. 34, 1499 (1961)
5. F.F. Carlson, G.J. King, and B.S. Miller, Hyperfine Structure of F-Center Spin Resonance in Sodium Azide, J. Chem. Phys. 33, 1266 (1960)
6. L.D. Bogan, R.H. Bartram, and F.J. Owens, A Model for Room Temperature Color Centers in Potassium Azide, Bull. Am. Phys. Soc. II 15, 370 (1970)
7. H.G. Heal, and J.P.S. Pringle, Color Centers in X Irradiated Metal Azides, J. Phys. Chem. Solids 15, 261 (1960)
8. P.W.M. Jacobs, and F.C. Tompkins, The Photolysis of Solid Potassium Azide, Proc. Roy. Soc. (London) A215 254 (1952)
9. D.A. Wiegand, Defect Formation in Inorganic Azides, Bull. Am. Phys. Soc. 14, 1187 (1969)
10. D.A. Wiegand, Photoproduction of Imperfections in Crystalline Lead Azide, Bull. Am. Phys. Soc. 15, 371 (1970)
11. A.C. McLaren, The Absorption Spectra of Single Crystals of Pure and Partially Decomposed Silver Azide, Proc. Phy. Soc., London B70, 147 (1957)
12. D.S. Downs, and F.J. Owens, ESR Identification of NO in X-Ray Irradiated $Ba(N_3)_2$, Bull. Am. Phys. Soc. II, 15, 313 (1970)

13. W. Garrett, Crystal Growth and Photolytic Decomposition of Lead Azide, Bull. Am. Phys. Soc. II, 15, 298 (1970)
14. Mott & Gurney, Electronic Processes in Ionic Crystals, Oxford University Press (1948)
15. M. Barkey, and T. Gora, private communication
16. Van De Hulst, Light Scattering by Small Particles, John Wiley & Sons, Inc. (1957)
17. J.H. Schulman, and W.D. Compton, Color Centers in Solids, The MacMillan Co., New York (1962)
18. P.O. Johnson, Absolute Optical Absorption from Diffuse Reflectance, J. of Opt. Soc. Am. 42, 978 (1952)
19. B.S. Miller, Identification of Colloidal Sodium in Sodium Azide, J. Chem. Phys., 33, 889 (1960)
20. R.C. McMillan, Electron Spin Resonance of Potassium Colloids in KN_3 , J. Phys. Chem. Solids 25, 773 (1964)
21. D.A. Wiegand, and R. Smoluchowski, The Production of Defects in Crystalline Alkali Halides by Ionizing Radiation, The Chemical and Biological Actions of Radiation (journal), 7, 166 (1964)

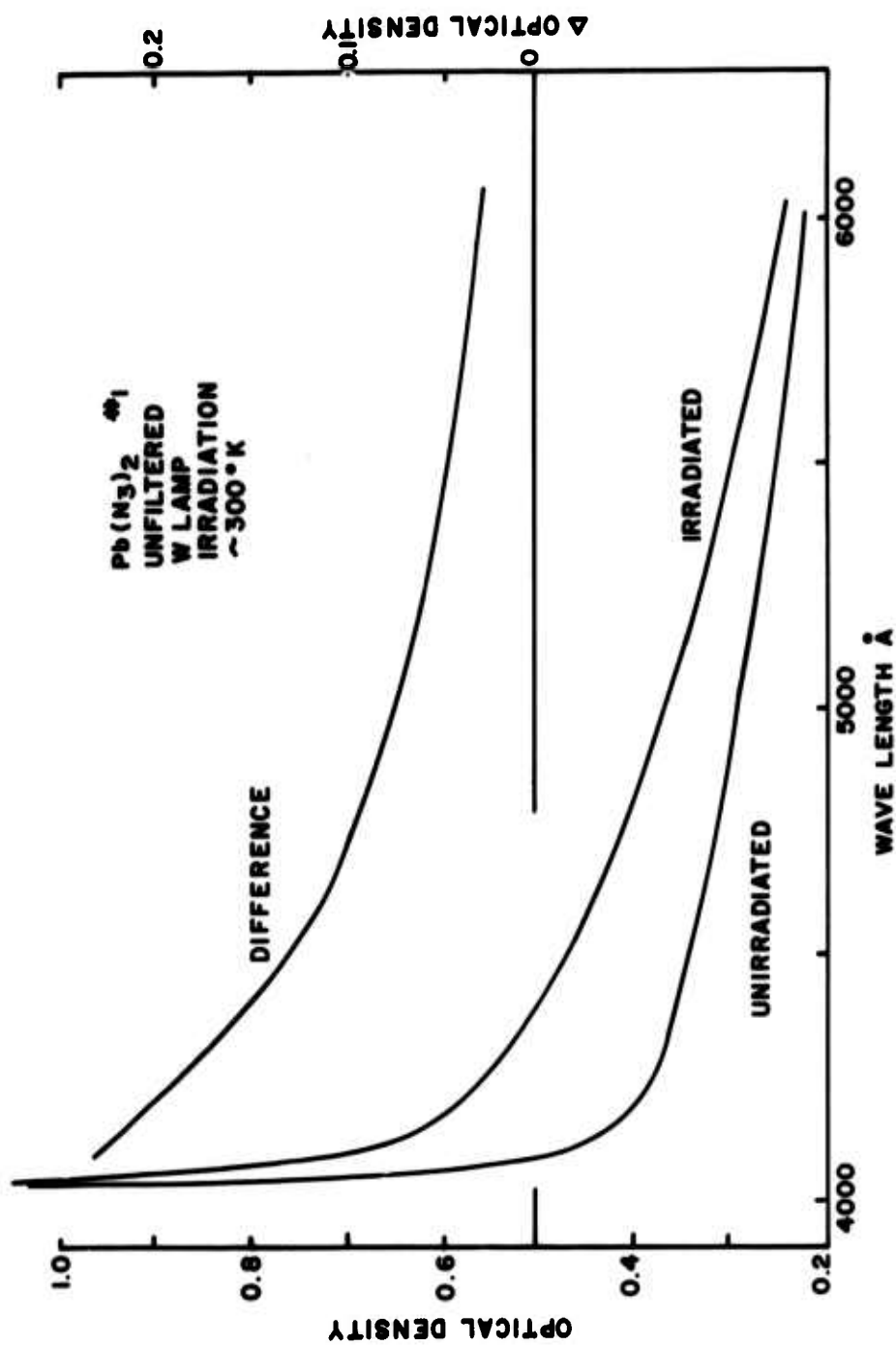


Fig 1 Optical density of unirradiated and irradiated $\text{Pb}(\text{N}_3)_2$ vs wavelength λ . The difference in optical density vs λ is also given.

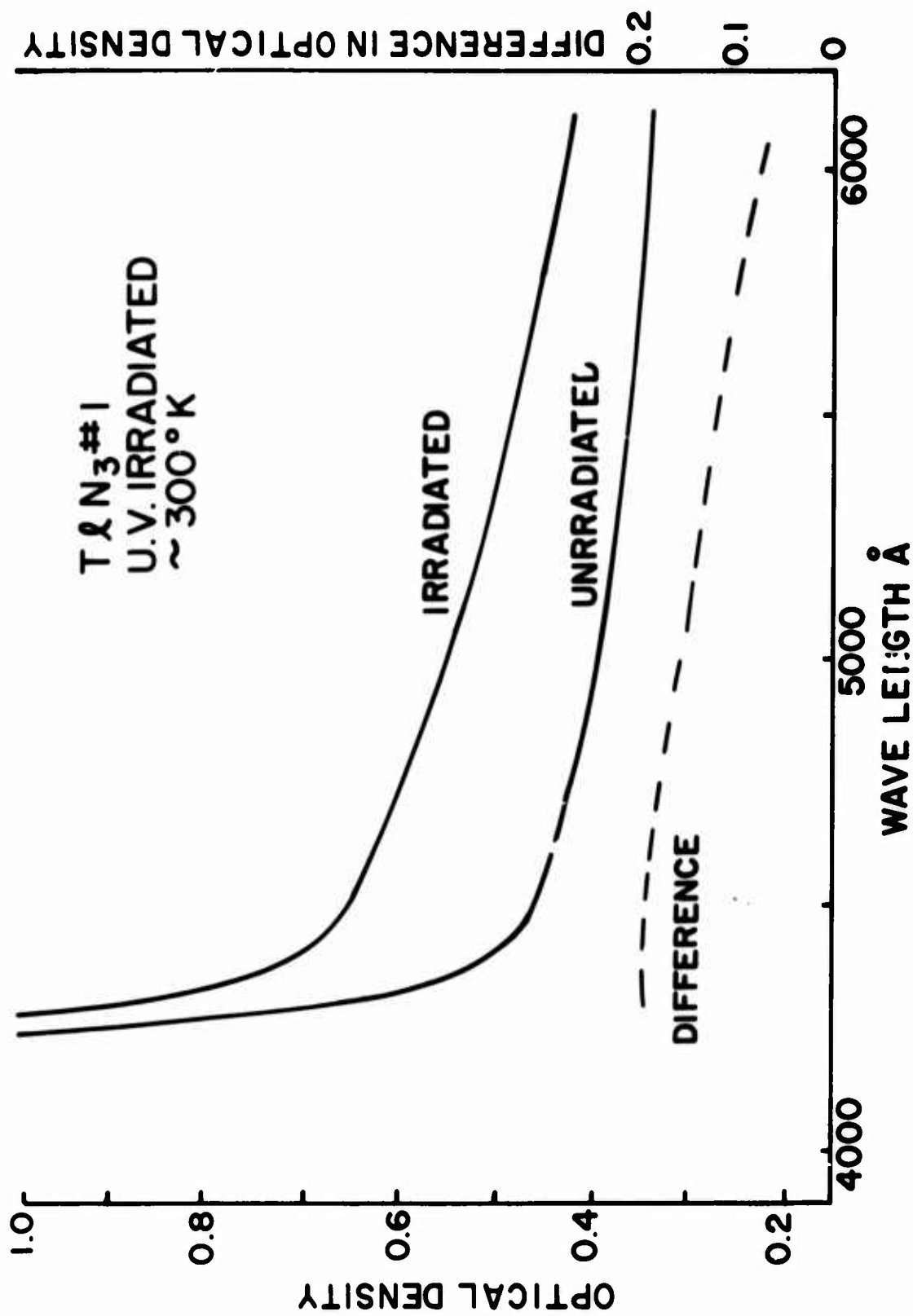


Fig 2 Optical density of unirradiated and irradiated TlN₃ vs wavelength λ . The difference in optical density vs λ is also given.

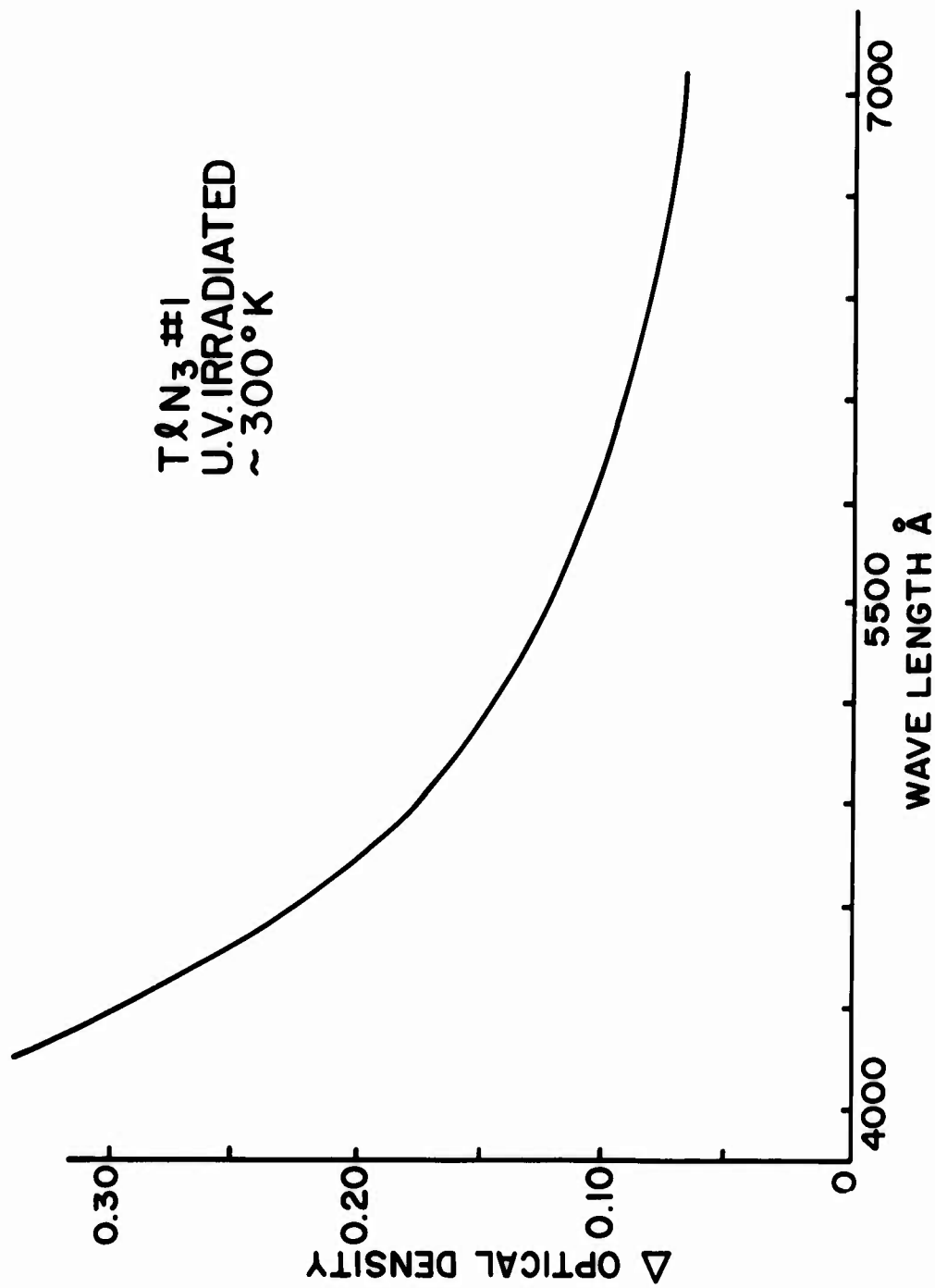


Fig 3 Change in optical density due to irradiation vs wavelength for TlN₃

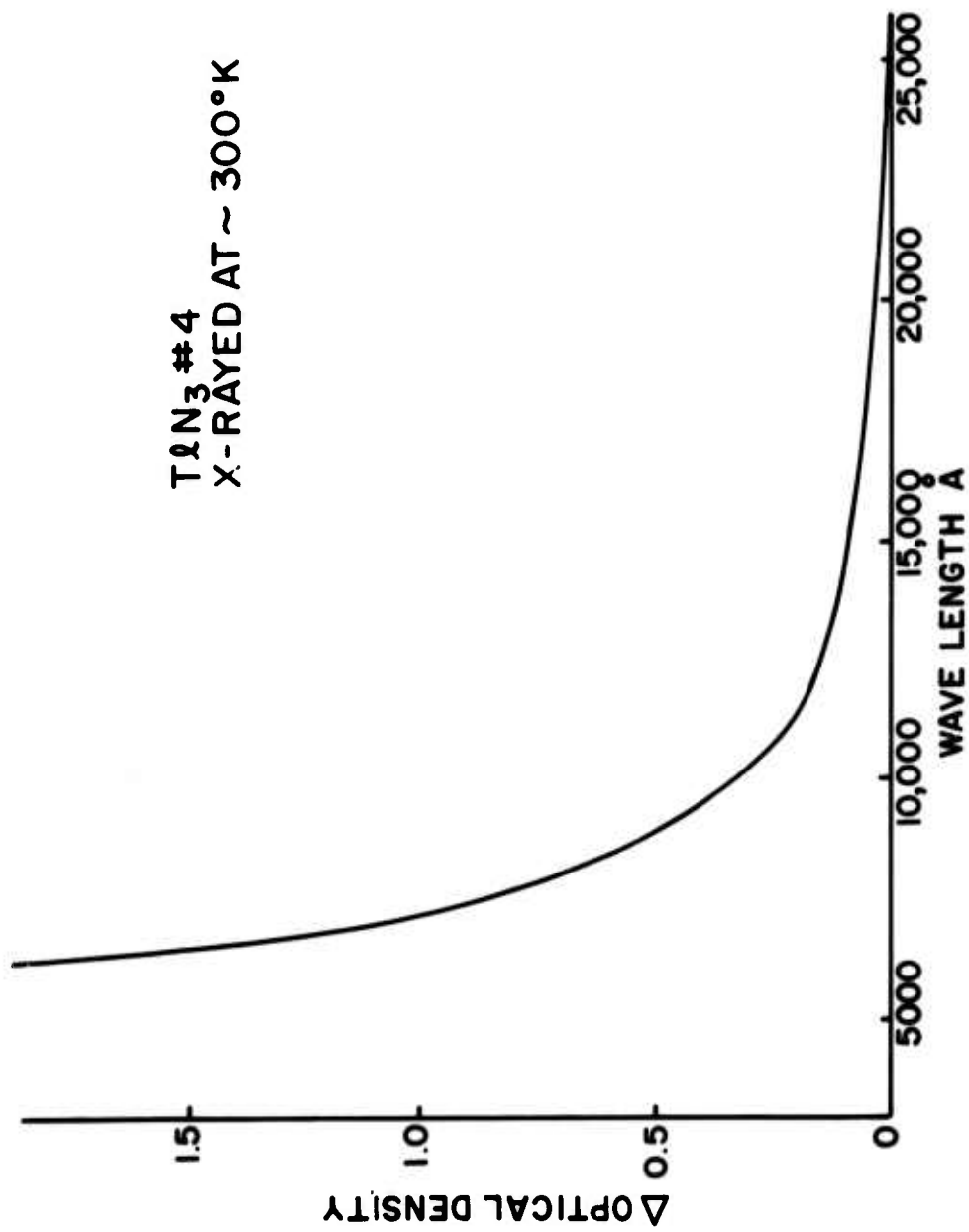


Fig 4 Change in optical density vs wavelength for x-irradiated TlN₃

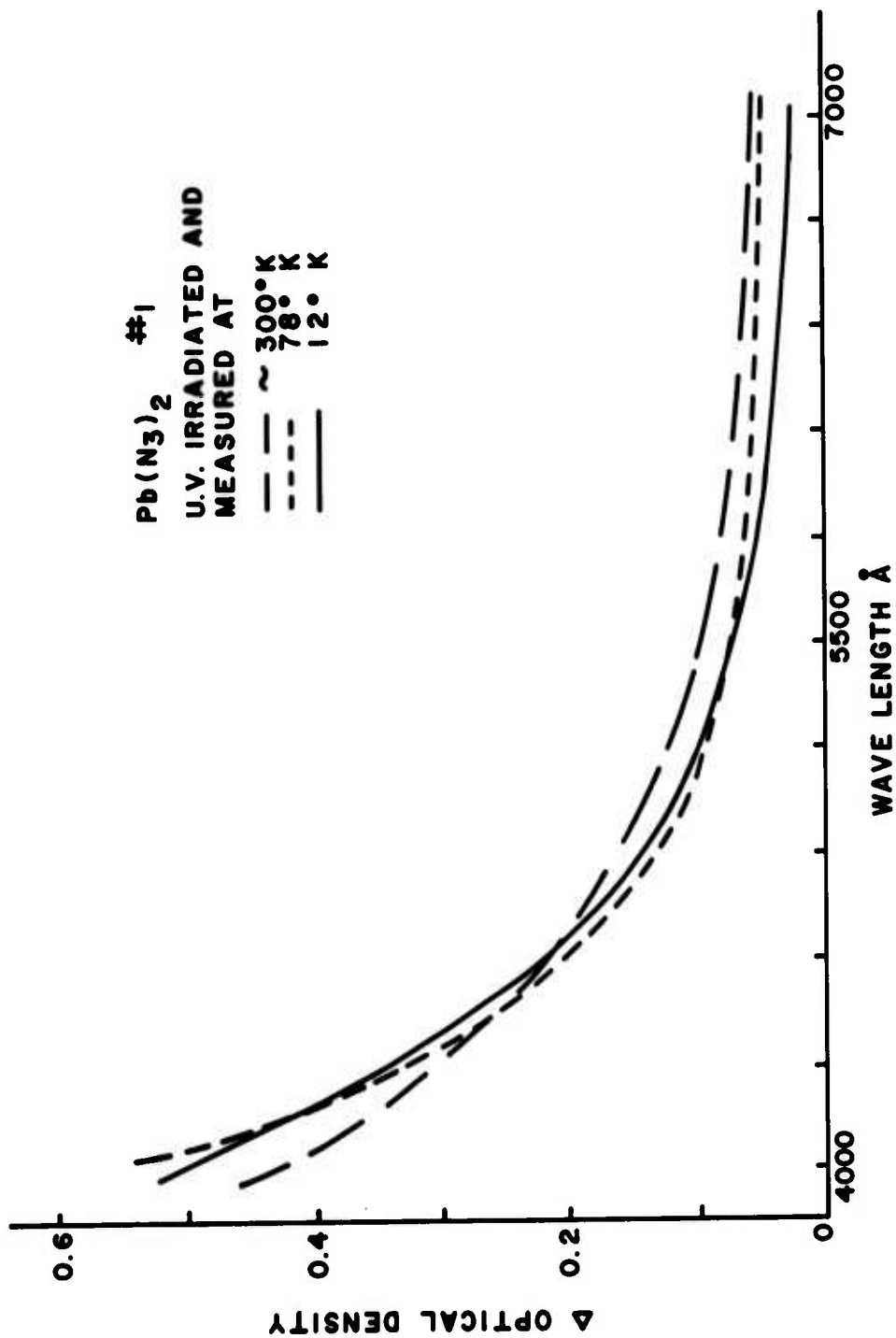


Fig 5 Change in optical density vs wavelength due to ultraviolet irradiation of $\text{Pb}(\text{N}_3)_2$ as a function of sample temperature during irradiation

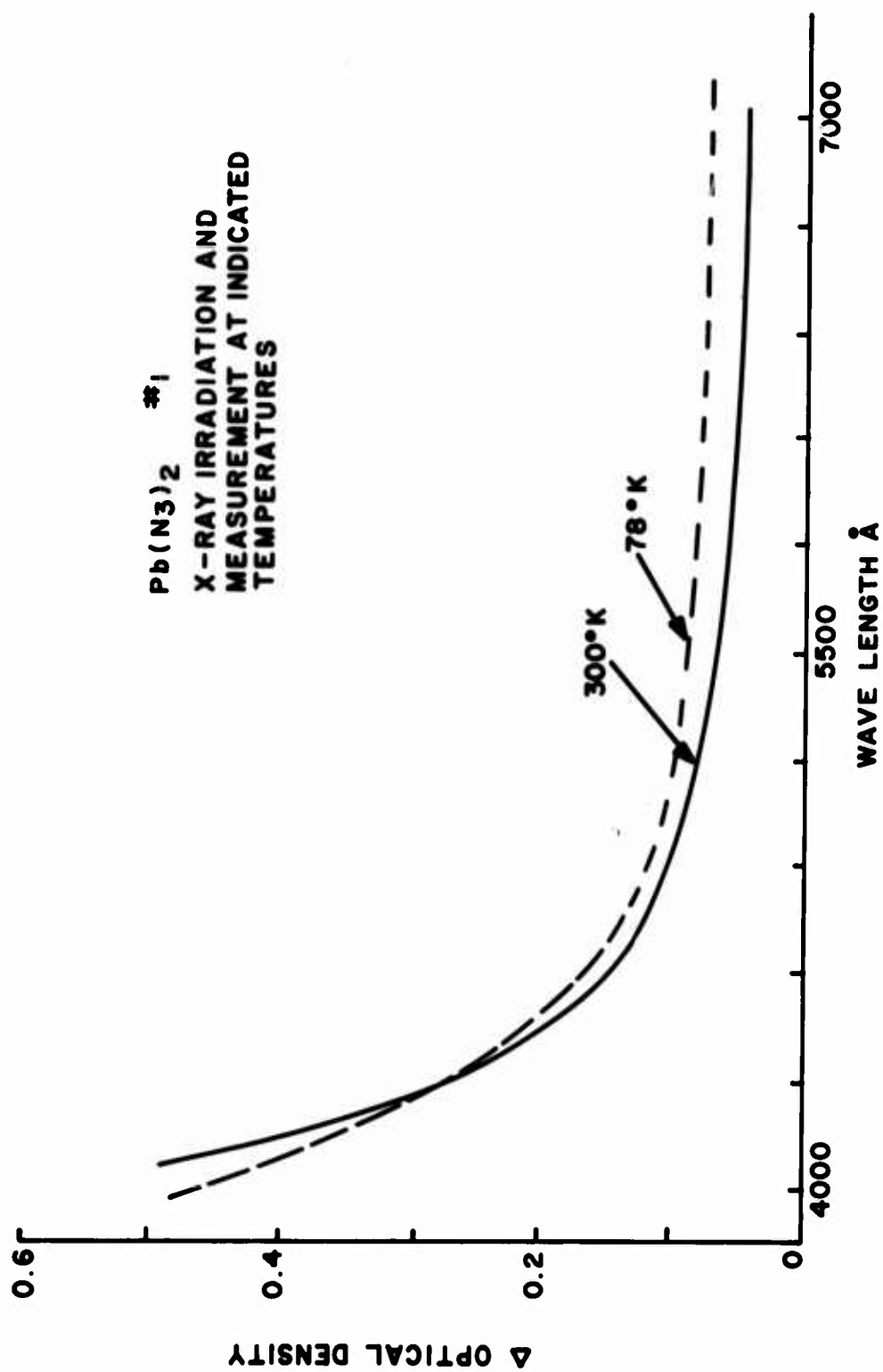


Fig 6 Change in optical density vs wavelength due to X-irradiation of Pb(N₃)₂ as a function of sample temperature during irradiation

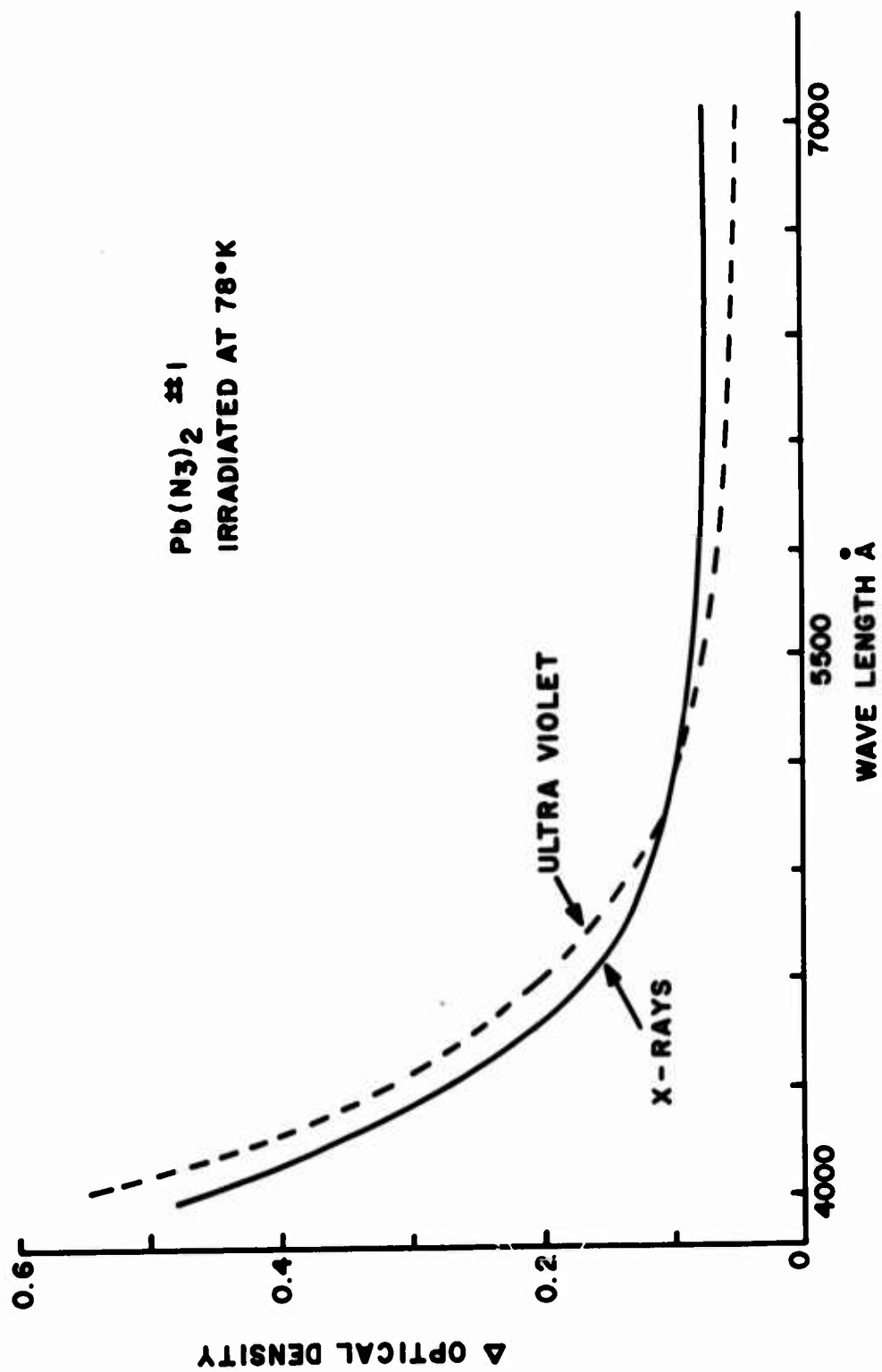


Fig 7 Change in optical density vs wavelength for Pb(N₃)₂ exposed at 78°K

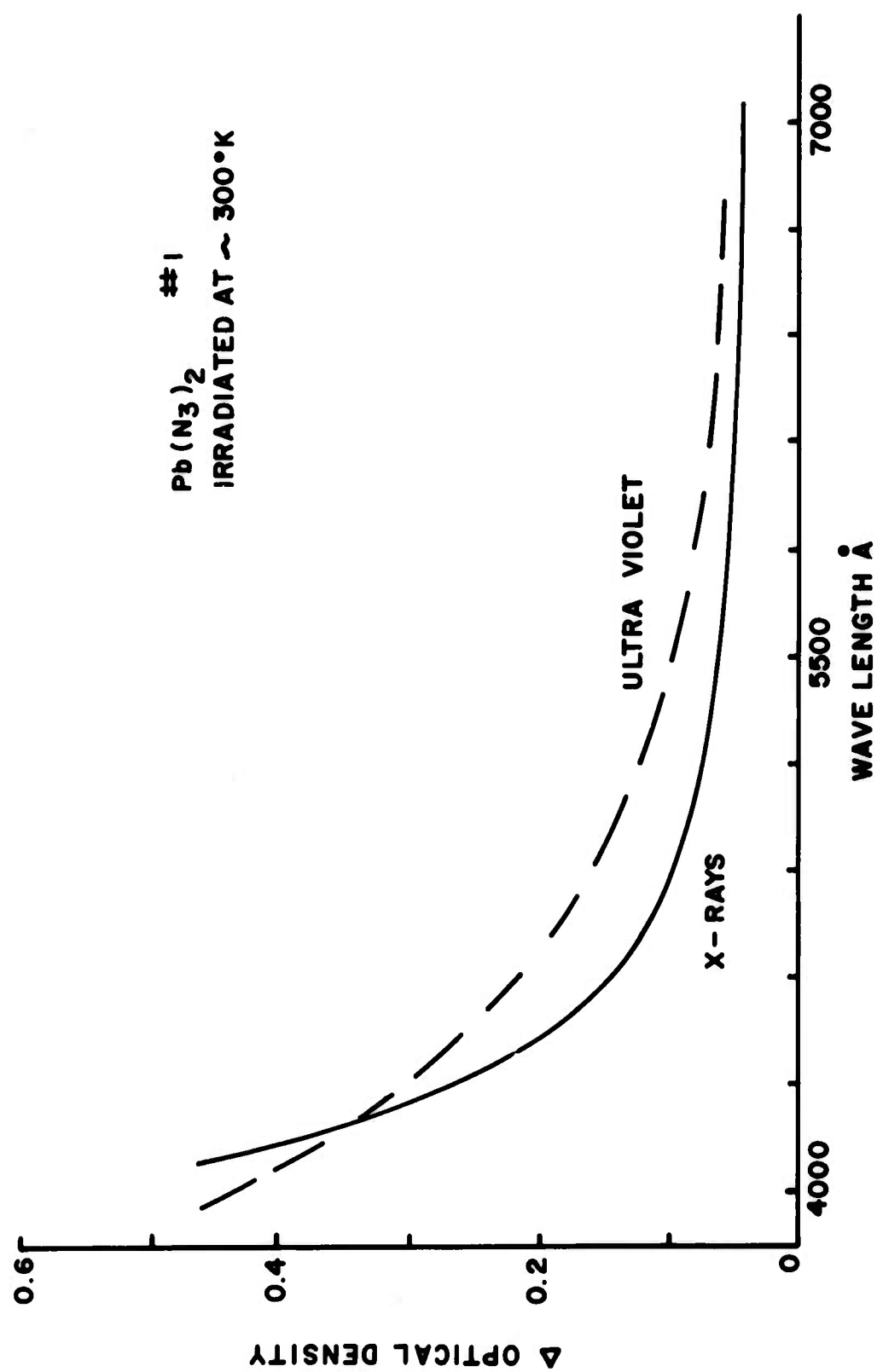


Fig 8 Change in optical density vs wavelength for Pb(N₃)₂ exposed at 300°K

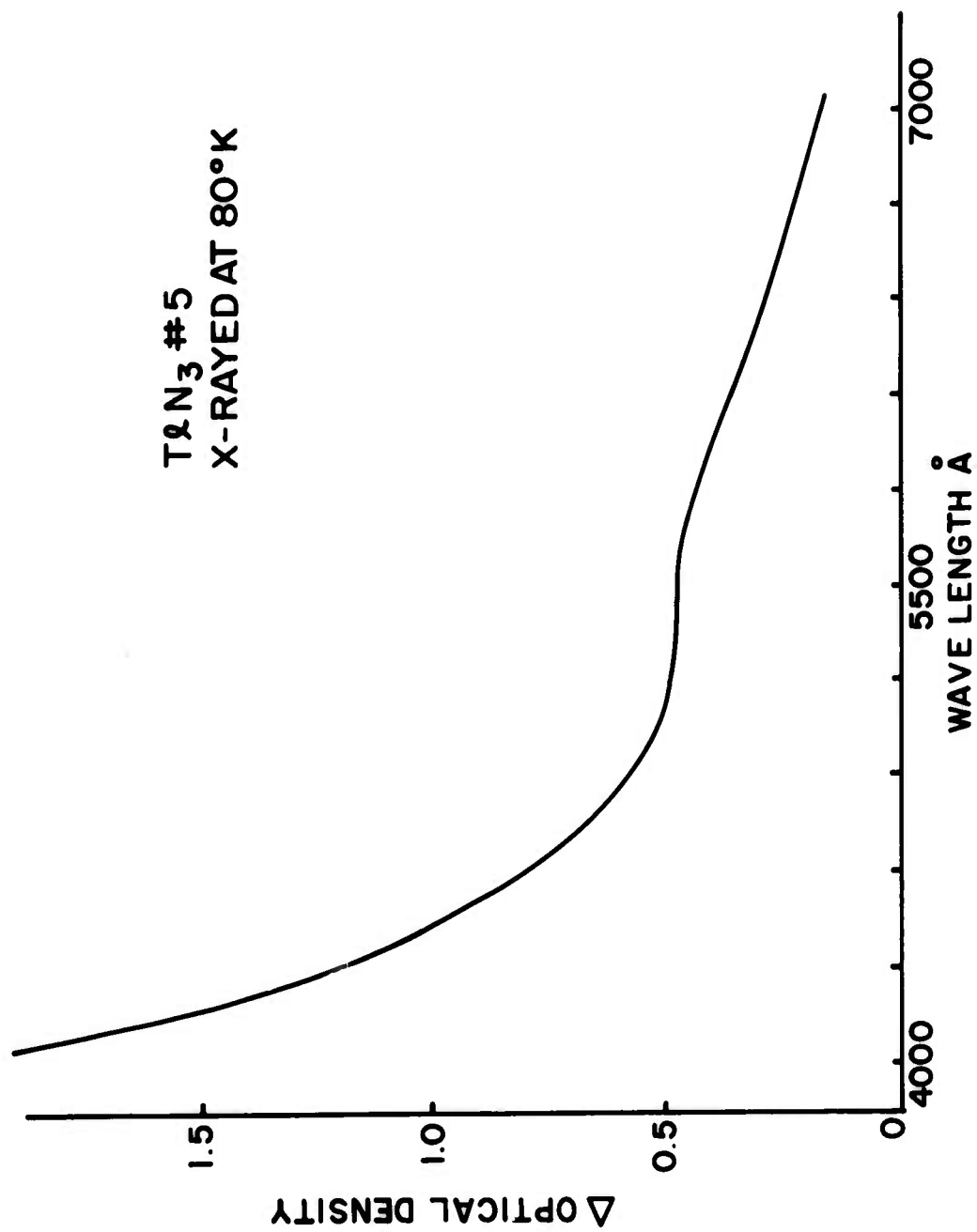


Fig 9 Change in optical density of TlN₃ due to X-irradiation at 80°K

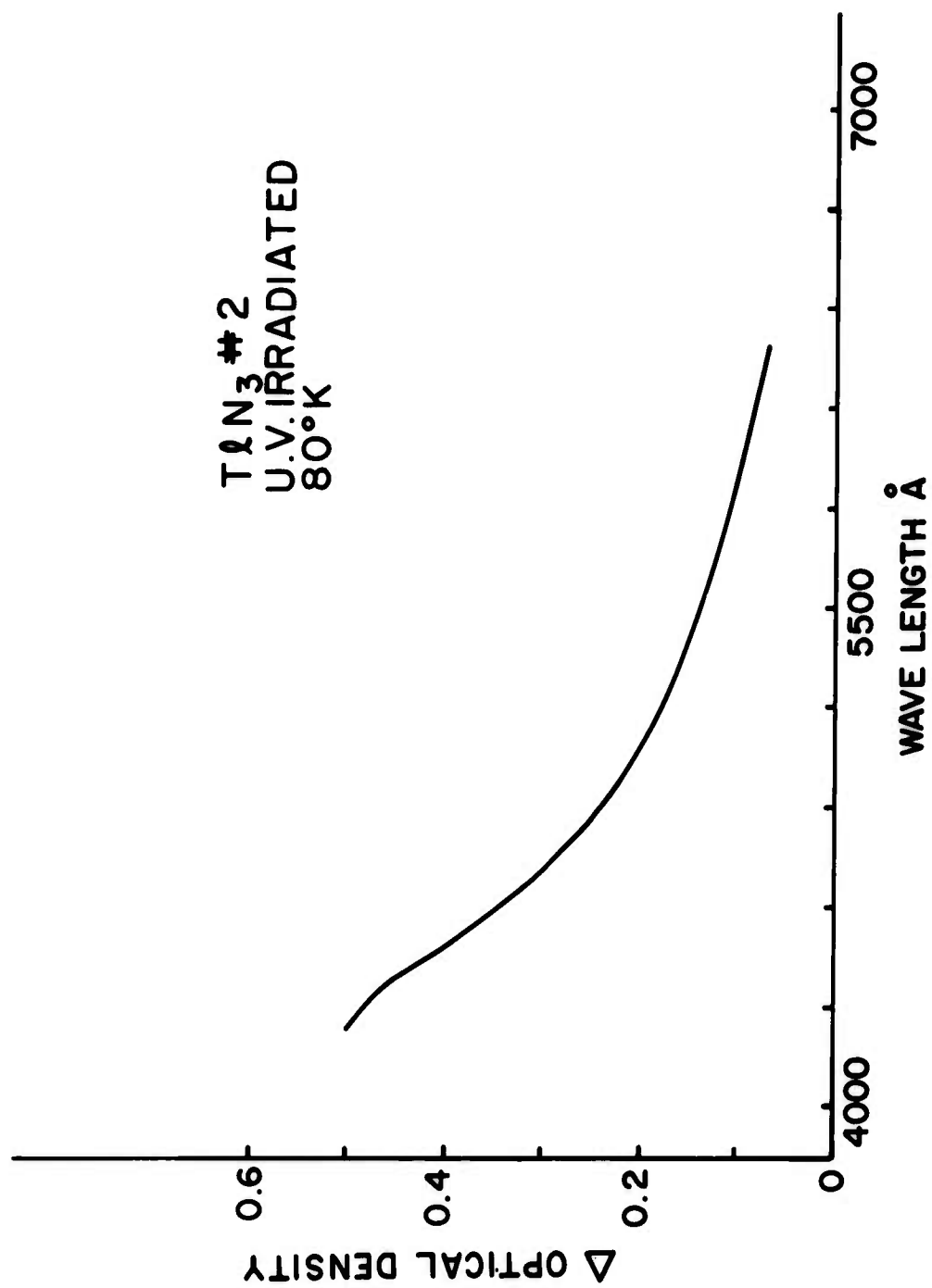


Fig 10 Change in optical density of TlN₃ due to ultraviolet irradiation at 80°K

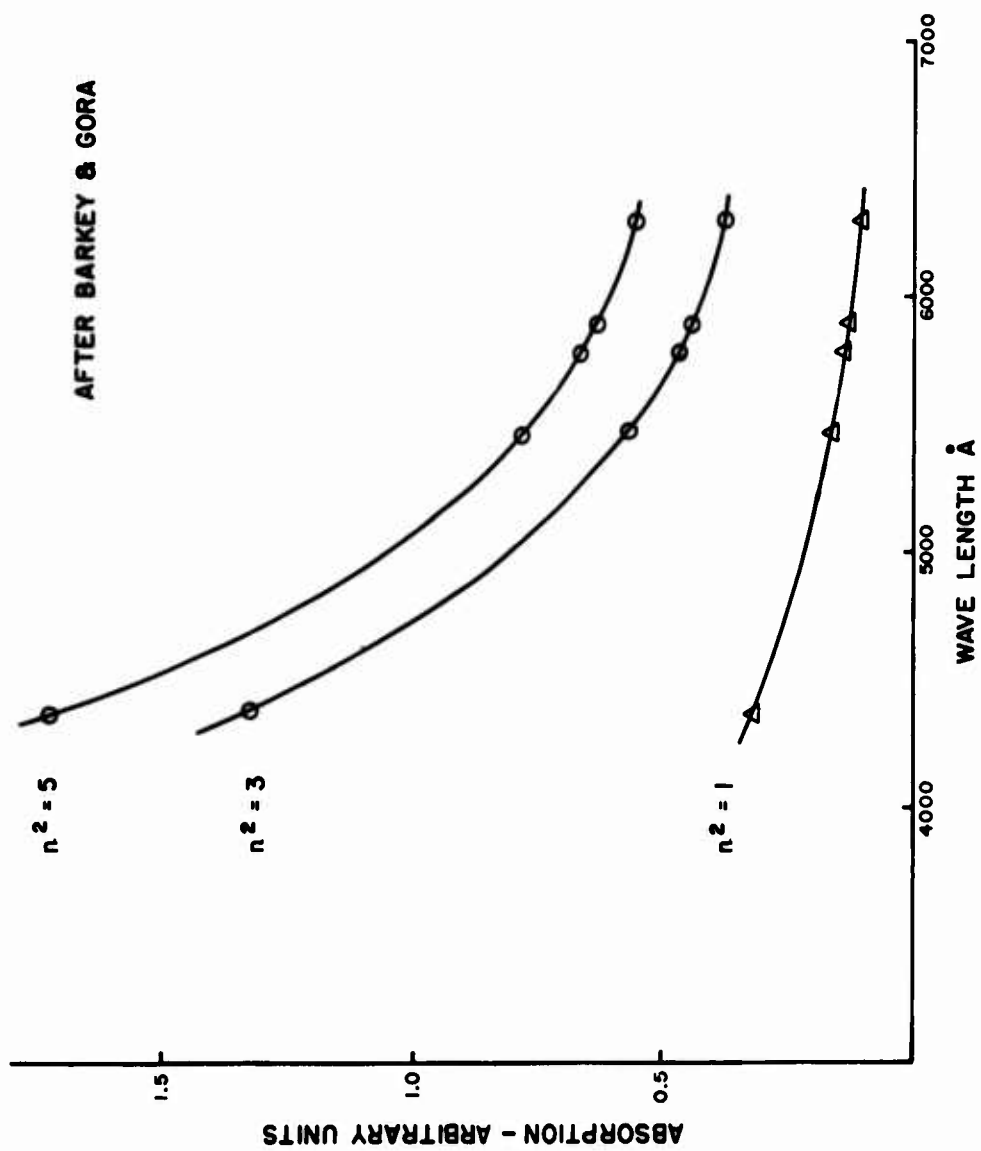


Fig 11 Absorption in arbitrary units vs wavelength for colloidal Pb as a function of the square of the index of refraction of the surrounding material

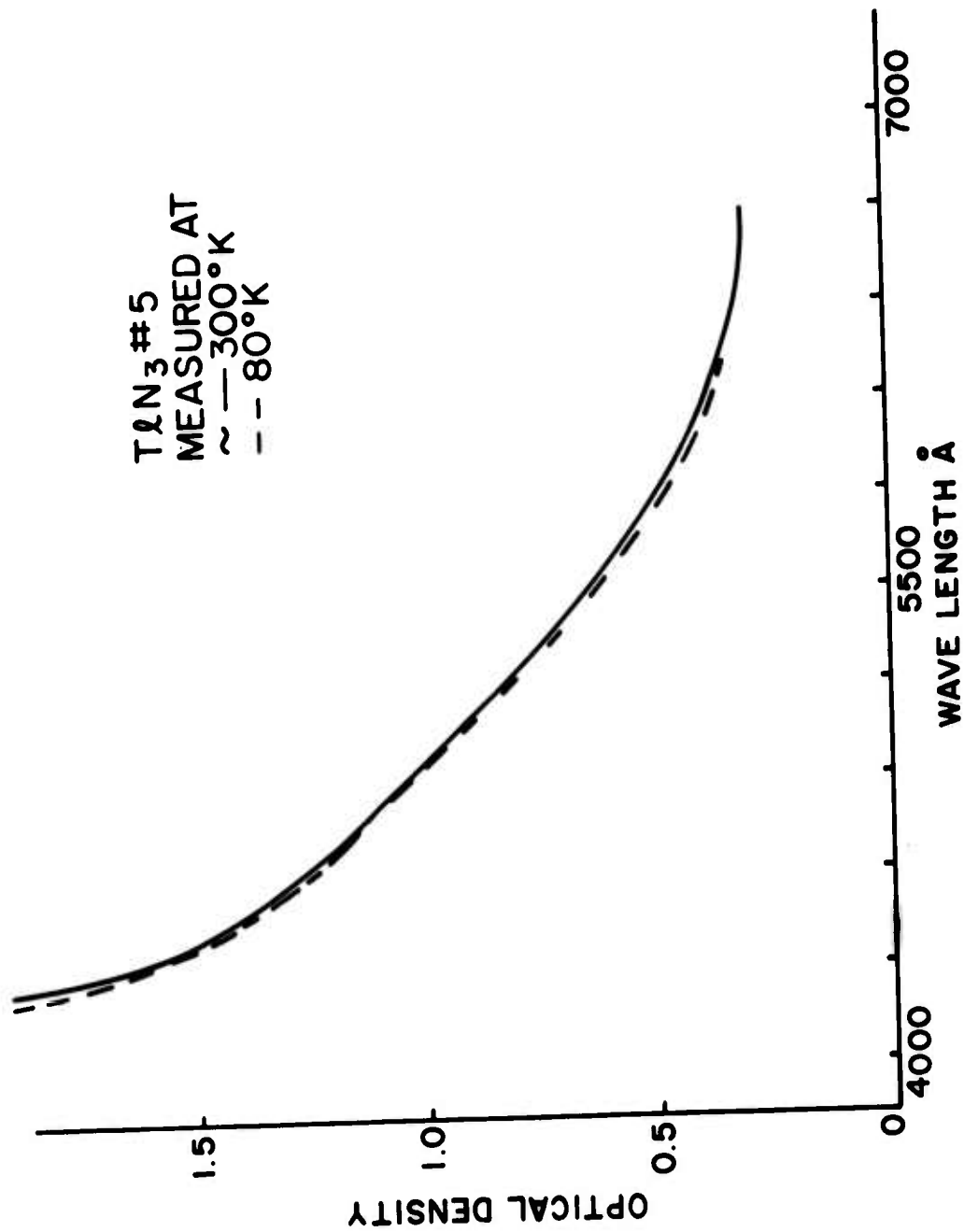


Fig 12 Optical density vs wavelength for TlN₃ irradiation at 80°K

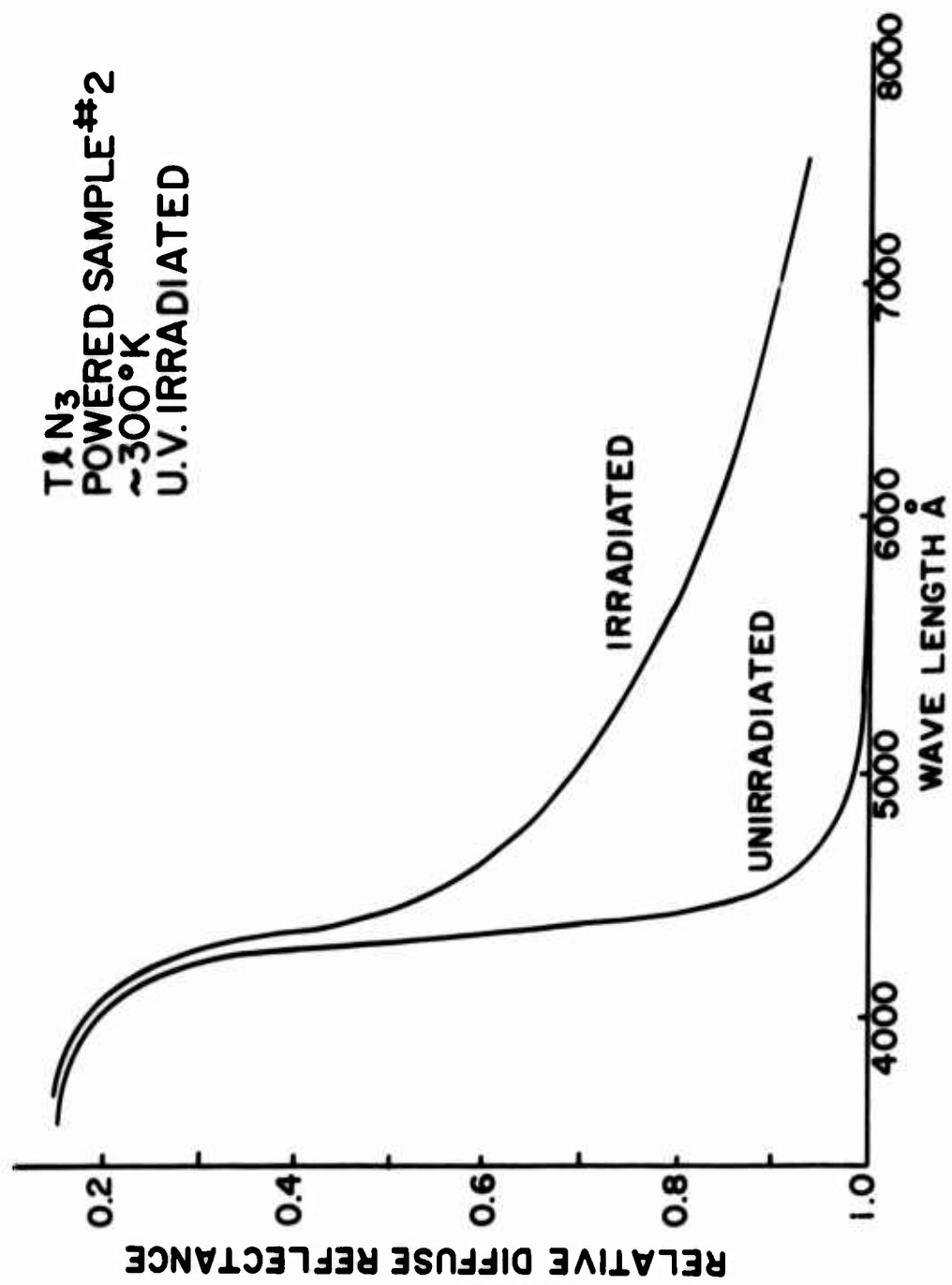


Fig 13 Diffuse reflectance vs wavelength for powdered TiN₃

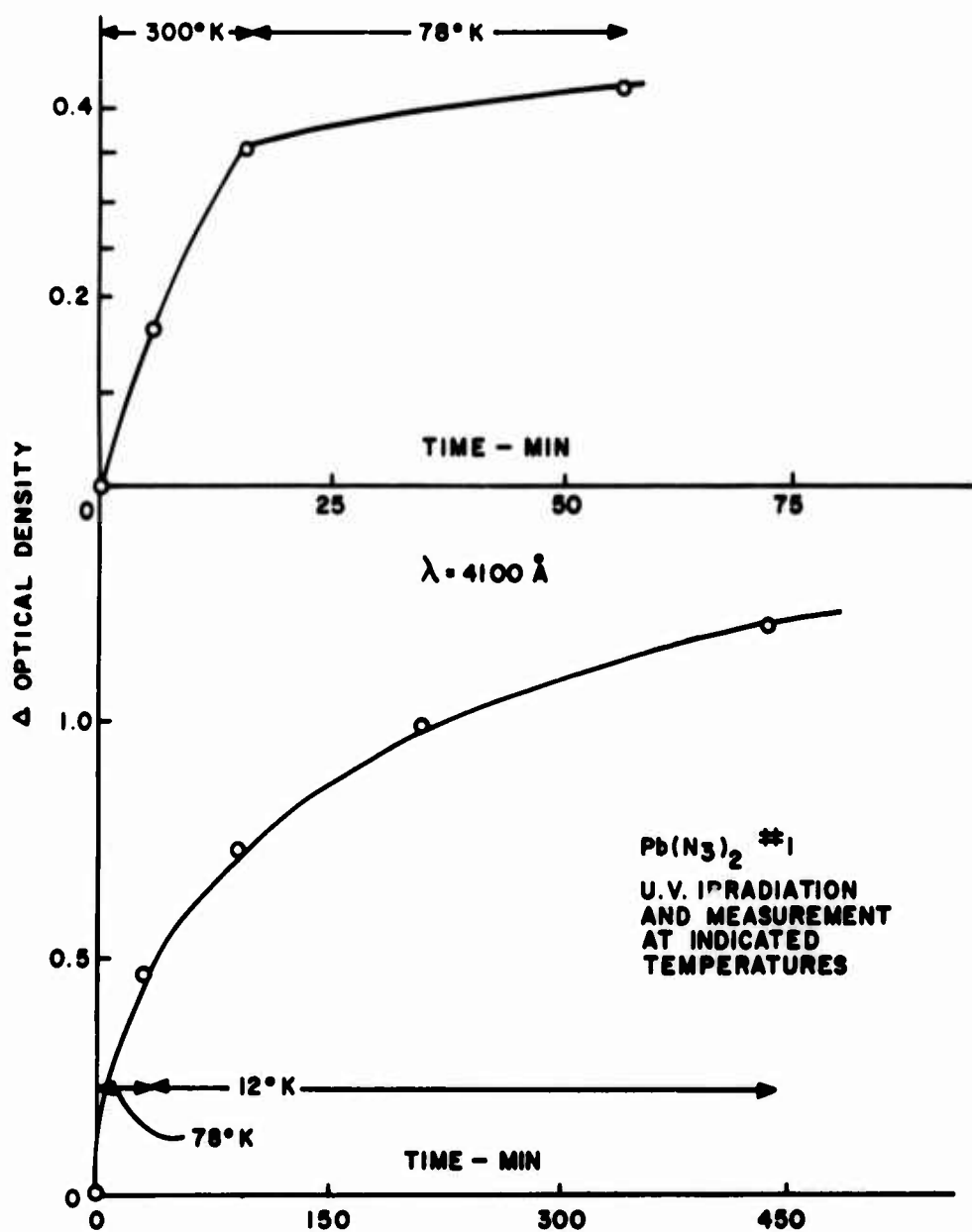


Fig 14 Change in optical density vs irradiation time as a function of sample temperature. Ultraviolet irradiation

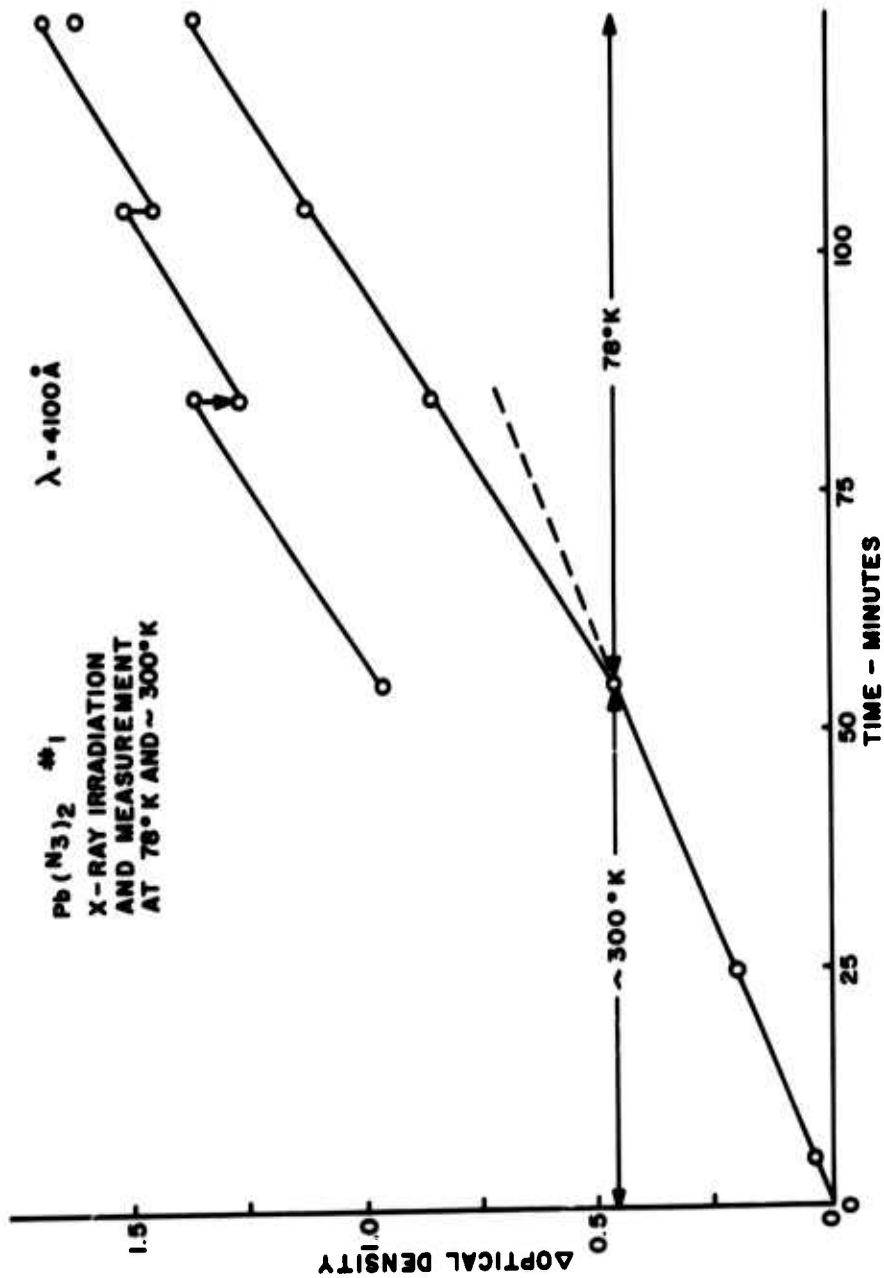


Fig 15 Change in optical density vs irradiation time as a function of sample temperature. X-ray irradiation. The vertical arrow at the upper right curve indicates annealing at 78°K during non-irradiation periods. The same data is plotted without the annealing in the lower right curve.

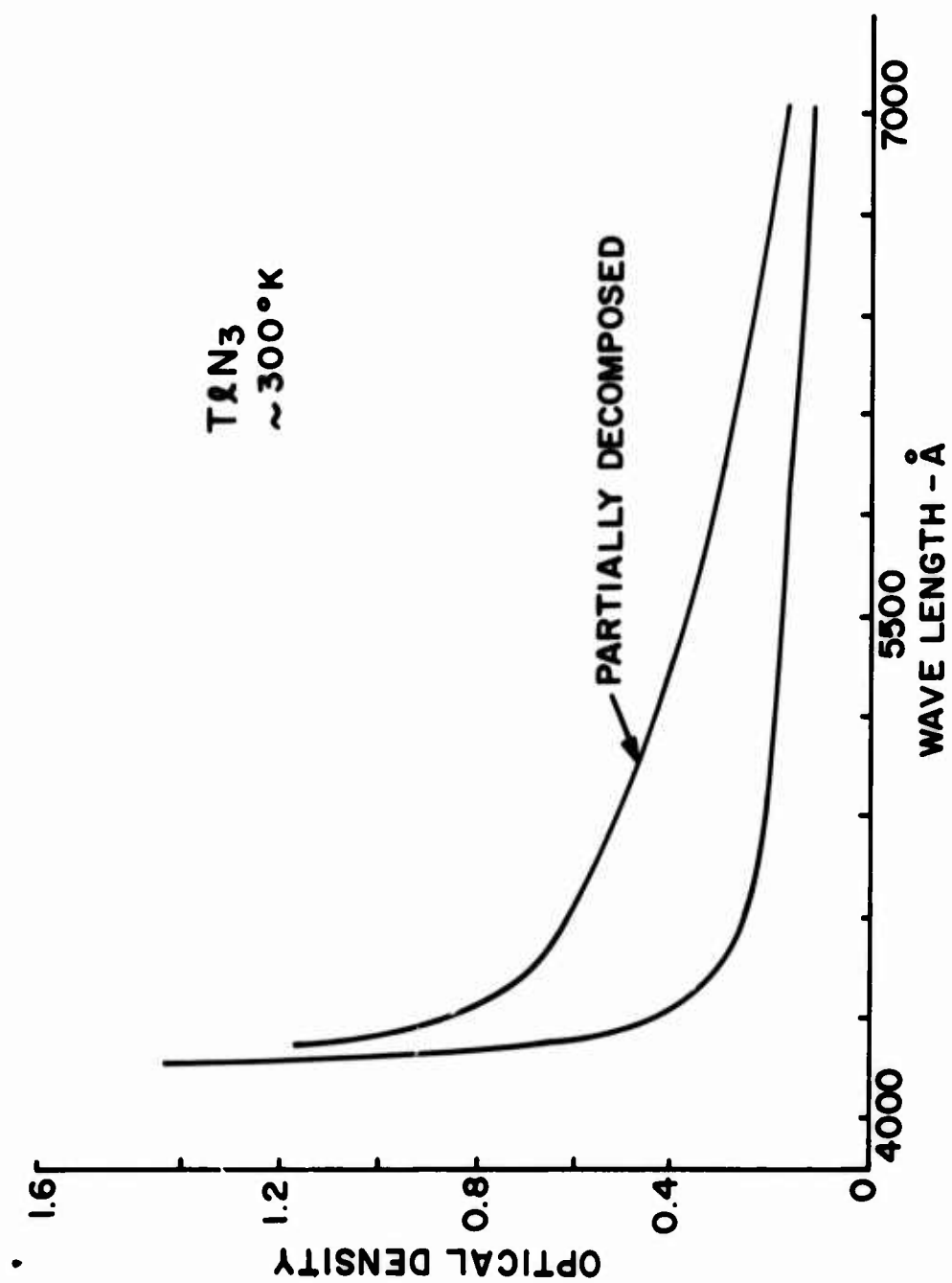


Fig 16 Optical density vs wavelength for TiN₃ before and after heat treatment

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DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) Picatinny Arsenal, Dover, New Jersey 07801		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
		2b. GROUP
3. REPORT TITLE PHOTOPRODUCTION OF DISORDER IN $Pb(N_3)_2$ and TlN_3		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
5. AUTHOR(S) (First name, middle initial, last name) D. A. Wiegand		
6. REPORT DATE December 1970	7a. TOTAL NO OF PAGES 42	7b. NO. OF REFS 21
8a. CONTRACT OR GRANT NO. b. PROJECT NO. 1T061102A32B c. AMCMS Code 501B.11.856 d.		9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report 4080 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY
13. ABSTRACT Pb, Tl, and other inorganic azides have been exposed to ultraviolet and X-ray irradiation, and the resulting changes in optical properties have been studied. This irradiation was found to produce structureless increase in extinction, which increases in magnitude with decreasing wavelength to the band edge. Calculations for $Pb(N_3)_2$ indicate that the wavelength dependence of this irradiation-induced extinction is what might be expected from colloidal lead. The increased extinction is insensitive to the temperature of observation, and diffuse reflectance measurements indicate that some part, if not all of it, is due to absorption. Both of these results are to be expected if the extinction is due to colloidal lead. Essentially the same type of extinction is obtained for ultraviolet and X-ray irradiation at sample temperatures of 12° , 78° , and $\sim 300^\circ K$, and also for decomposition produced solely by thermal means. Some differences between $Pb(N_3)_2$ and TlN_3 are discussed.		

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14 KEY WORDS	LINK A		LINK B		LINK C	
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Inorganic azides						
Inorganic halides						
Colloidal metal						
Heavy metal azides						
Ultraviolet irradiation						
X-ray irradiation						
Optical extinction						
Optical absorption						
Optical scattering						
Point imperfections						
Point defects						
Irradiation-induced disorder						
Optical density						
Reflectance						
Spin resonance						
Spectrophotometer						
Particle size						
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Electrons						
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